

“The Properties of the Aluminium-Tin Alloys.” By W. CARRICK ANDERSON, M.A., D.Sc., and GEORGE LEAN, B.Sc. Communicated by Professor H. A. MIERS, F.R.S. Received June 16,—Read June 18, 1903. Received in revised form August 8, 1903.

[PLATE 15.]

Aluminium and tin may be melted together in all proportions to give uniform fluid mixtures. The melting cannot be done in the ordinary fireclay or plumbago crucibles, since the admixture of tin appears to increase greatly the power which aluminium has to reduce the silicates of fireclay, the reduced silicon becoming absorbed in the body of the metal. In our earlier experiments on these alloys we learned that, even with careful melting at a temperature not higher than about 750°C ., it was impossible to prevent this rapid reduction of silicon. In a few minutes the alloys became badly contaminated with the metalloid; in one instance as much as 11 per cent., partly crystalline and partly amorphous, was found in the cooled ingot. On this account the metal was in our subsequent experiments invariably melted in small crucibles of baked carbon. These were packed by means of asbestos inside fireclay crucibles of the ordinary Battersea type. The ingots made in this way were found to be uncontaminated, and contained only traces of silicon and iron from the aluminium employed, which was the best quality Foyers product. The weight of metal used in each experiment was from 10 to 40 grammes.

Cooling Curve.

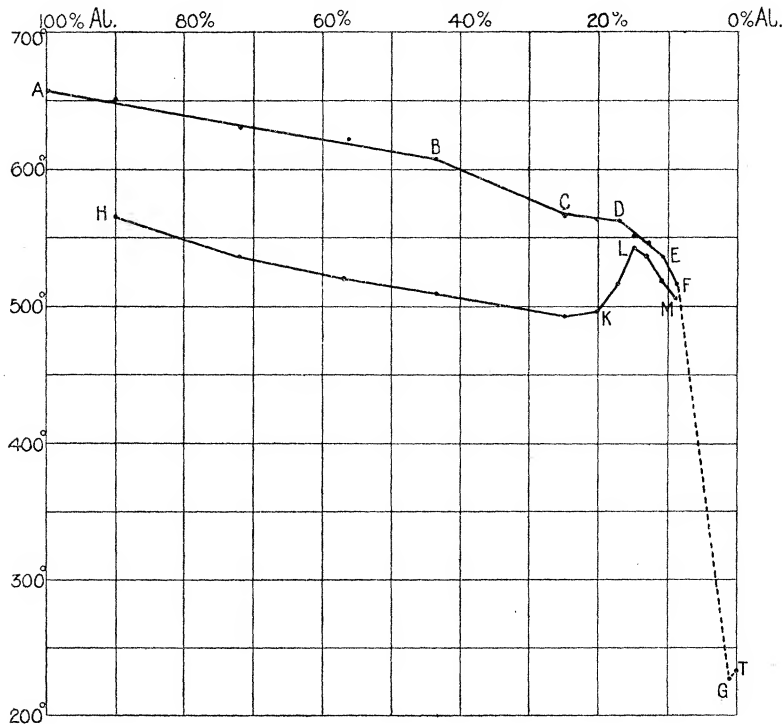
In a preliminary paper on the nature of these alloys, read before the British Association at its Glasgow Meeting in 1901,* we showed that above the eutectic limit the cooling curve of each alloy always reveals two breaks. The general form of the curve is as we then stated it to be. It has the usual extended form corresponding to the gradual separation of mixed crystals from the solution during cooling, and the first break point is continuously lowered with every increment of tin. The second break, which marks the solidifying point of the eutectic, we were at first inclined to place at 232° , or very little below that temperature. More careful working, however, with a larger number of alloys, has enabled us now to place it nearer the figure originally stated by Heycock and Neville,† and rather under it, viz., 228° — $228^{\circ}5$.

* ‘B. A. Rep.,’ 1901, p. 606.

† ‘Journ. Chem. Soc.,’ 1890, p. 376.

The curve shown in Diagram 1 is obtained by means of a direct-reading Le Chatelier pyrometer. The platinum-rhodium couple was wrapped in a thin covering of asbestos paper, worked into a pulp and dried, and then placed in the thoroughly liquid mixtures of aluminium and tin. The quantities of metal used were the same throughout, and the conditions of experiment were arranged so that the radiation was similar in each case. The curve ABCDEF shows the position

DIAGRAM 1.—Aluminium-Tin Alloys.



of the first halt in the cooling curves of the alloys lying between 100 per cent. aluminium and 9 per cent. aluminium. It is, therefore, the liquidus curve, or freezing-point curve. In each experiment the point of temperature was noted at which the retardation of the fall in temperature ceased and the rate of cooling became once more normal. These temperatures are plotted on the line HKLM, which may, therefore, be regarded as approximating to the points at which active separation of solid matter ceased in each of the alloys. It thus indicates the trend of the solidus curve of the series.

The positions occupied by this first break point in the several alloys

which we examined makes the freezing-point curve connecting these a peculiar one. With the exception of a slight deviation which is apparent at the point B (see curve Diagram 1), it slopes uniformly downwards until about 25 per cent. of aluminium is present (point C on curve). From this point, however, until the percentage of aluminium reaches 17 per cent. (D on curve), the temperature at which the first break occurs remains practically constant. Indeed, when uniformity in the conditions of cooling is maintained, the alloys from 25 per cent. aluminium to 17 per cent. aluminium may be said to begin the separation of solid matter at almost exactly the same temperature, namely 561° C. When the percentages of aluminium are less than 17, the downward trend of the curve is resumed at a more rapid rate than before, with perhaps a slight further deflection at or about the point E in our diagram.

In our experiments the flattening of the curve extended from the alloy having the composition 24.8 per cent. aluminium to that containing 17.43 per cent. Between these limits the first signs of heat evolution appeared at from 563° to $560^{\circ}.5$ C. A definite compound of the formula AlSn would have the composition

Al.....	18.5 per cent.
Sn.....	81.5 „

Whether the solid matter separating out at the temperature stated has this composition or not, it is at least the case that in that part of the curve to the left of this point the separation is taking place from a solution containing more than one atom of aluminium to each atom of tin; to the right it is taking place from a solution in which atoms of tin preponderate. The homogeneous liquid mixtures, therefore, to the left are solutions of tin in aluminium, those to the right are solutions of aluminium in tin.

A freezing-point curve for these alloys has already been given by H. Gautier.* His results differ from ours most markedly in this, that in the region CD he finds the separation of solid matter to commence at temperatures higher than is the case in alloys both to the left and right of it. The result is a very pronounced "kink" in the curve, which in our experiments is represented to the extent of only 1° C. in the case of the alloy containing 17.43 per cent. of aluminium. The explanation of the difference is doubtless to be found in the different rates of cooling in the two series of observations. For the sake of comparison we append the figures. The melting point of aluminium is given by Gautier as 650° C.; we have chosen the figure 655° C.

* 'Comptes Rendus,' vol. 123, 1896, p. 109.

Gautier.		Carrick Anderson and Lean.	
Per cent. of Al.	Temp. of separation. °C.	Per cent. of Al.	Temp. of separation. °C.
100	650	100	665
83	637	90·01	649
70	622	71·93	630
54	605	56·63	622
27	558	43·50	608·5
20·5	553	24·80	563
19·0	565	20·20	560
15·7	580	17·43	561
12·5	565	15·57	549
8·5	520	13·31	544
7·0	500	10·65	537
5·5	470	8·33	515
2·4	390		
1·0	328		
0·05 (0·5 ?)	229	0·5	228—228·5
0·00	232	0·0	232

Action on Water.

A remarkable feature of the alloys of the aluminium-tin series, to which we directed attention in our previous paper, is the readiness with which they decompose water with evolution of hydrogen even at ordinary temperatures. The phenomenon is exhibited by every one of the long series of alloys we have prepared, and in all cases the action is greatly intensified by warming the water. In consequence of this action, polished plates left in even slightly damp air become in a few days strongly pitted, and when the phenomenon was mentioned by one of us to the late Sir W. Roberts-Austen, he recalled that certain alloys of these metals, which had been prepared at one time in the Mint and laid aside, were found after a period to have crumbled to powder. We have not noticed the effect so fully developed in any of our specimens, but some which have been for two years in loosely-corked tubes are now becoming swollen and distorted.

In the paper already quoted we stated that we had not then been able to obtain any concordant results for the evolution of hydrogen in the case of the different alloys that might show a connection between the hydrogen given off and the aluminium contained in the alloy. We experimented at the time on alloys cast in chilled moulds, and the same annealed for several hours at various temperatures in the region just below redness. The figures showed, however, that the cast metal always yielded more hydrogen than annealed specimens containing the same proportion of aluminium. In repeating the experiments the

cast alloys were annealed together for 20 hours at a temperature never varying more than a few degrees from 400° C. Filings were then taken from the specimens, and 0.5 gramme in each case was treated with water. The specimens were placed alongside one another in a water bath kept at 80°—90° C. Some of the experiments were continued for six weeks, but as the evolution of gas in the latter stages is very slight, the later ones were stopped at the end of four weeks, and any small residual evolution neglected.

The results obtained are shown below :—

	Composition of alloy.					
	71.93 per cent. Al.	56.63 per cent. Al.	51.8 per cent. Al.	43.73 per cent. Al.	20.2 per cent. Al.	8.33 per cent. Al.
Gramme atoms of Al. per 100 grammes alloy	2.65	2.09	1.91	1.614	0.745	0.308
C.cs. of dry H (at N. T. P.) per gramme of alloy	356	266	240	184	77	23.3
C.cs. H per 1/100 gramme atom Al.	134	127	125	114	103.7	75.6

Theoretically 1/100 gramme atom of aluminium evolves 334.5 c.c. of hydrogen at N.T.P. (Diagram 2.)

Examination of polished plates of the alloys after corrosion with water shows that the action begins round the edge of the areas of aluminium-rich constituent. Our experiments indeed go to show that the decomposition of water is entirely ascribable to this part of the alloy. We got, it is true, a slight evolution of hydrogen when small pieces of the more fusible, tin-rich constituent expressed from the alloys on heating were placed in water, but, as we shall show later, the composition of this exuded metal is not the same as the eutectic.

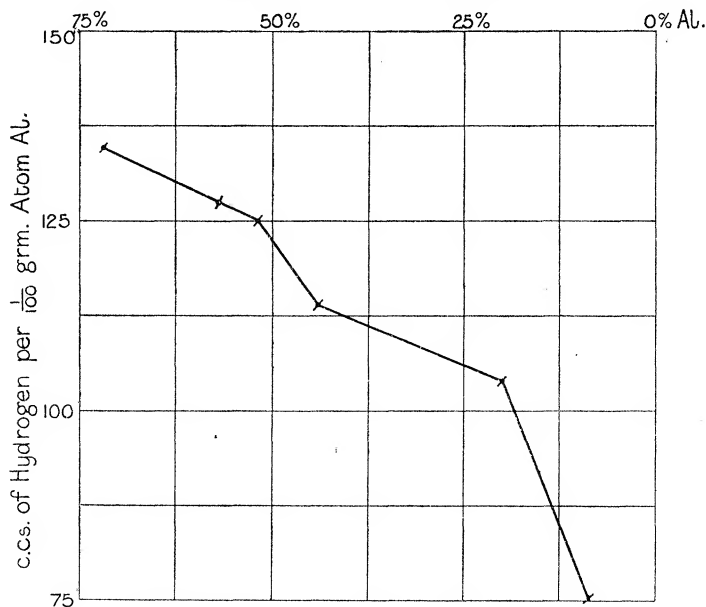
The photograph marked "1" illustrates the result of this water action continued for 124 hours at room temperature, on a polished plate containing 65 per cent. aluminium. The aluminium-rich areas have been worn down and corroded, leaving the tin-rich network in relief.

Microscopic Structure.

The microscopic structure of these alloys is illustrated by the accompanying photographs. The ingots were prepared as already described,

and were cast as before in a chilled mould. One half of the ingot was polished directly and etched for five minutes with a 2-per-cent. solution of caustic potash. The other half was annealed at 400° C. for twenty hours and then treated similarly. The two sets are referred to as the cast and annealed metals. The series examined ranged in composition from 99 per cent. aluminium to 1 per cent. When the percentage of aluminium exceeds that required to saturate the tin, which from our experiments is under 0.5, two constituents are always visible in the solidified alloy. One of these, easily recognisable as

DIAGRAM 2.—Hydrogen Evolutions.



that which solidified first, is abundant in those alloys which are rich in aluminium and decreases in quantity as the percentage of aluminium is lessened. In the cast metals, as illustrated in fig. 2, it is intimately mixed with the second constituent, which is the eutectic, until the aluminium has diminished to about 15 per cent., when it begins to appear in isolated patches in the eutectic. The exact freezing point of this eutectic mixture has been stated by Heycock and Neville to be 228.73° C. Annealing causes the constituent of higher melting point to segregate into patches, and the eutectic becomes then more clearly visible (fig. 3) even in alloys with a high percentage of aluminium. The lowest temperature at which this segregation takes place actively is above 250° and below 300° C. The photographs (figs. 4 and 5)

illustrate the process in the case of the alloy containing 15.42 per cent. of aluminium. No. 4 is a polished area of the cast metal. Heating in a current of dry hydrogen gas causes no marked rearrangement of the constituents at 216° — 220° C., even when continued for 28 hours. The polished surface, however, becomes roughened and presents a warty appearance. Similar results are produced when the experiment is repeated at $228\frac{1}{2}^{\circ}$ — 232° C., that is at a temperature just over the melting point of the eutectic. A more marked change is noticeable at 250° C., and a tendency to rearrangement is apparent, even after $9\frac{1}{2}$ hours at the temperature. Finally, when the annealing process is repeated at 290° — 300° for an equal time, $9\frac{1}{2}$ hours, the repolished and etched surface shows the structure of the alloy to have been profoundly modified thereby, and the appearance under the microscope is now that characteristic of the annealed metal (fig. 5). The round, oval, or sometimes irregular areas of aluminium-rich constituent, show up brilliantly white in the midst of the darker coloured eutectic. The eutectic is soft and on that account somewhat difficult to polish, but, if carefully treated and etched with a 2 per cent. caustic potash solution so as to remove the skin of smeared metal from the surface, it exhibits under a magnification of less than 200 diameters the wavy or striated structure characteristic of eutectic mixtures generally (fig. 6).

The polished and etched plates of these alloys, both cast and annealed, must be examined soon after they are prepared, since the surface rapidly becomes pitted, owing to the action of atmospheric moisture. In the annealed ingots this pitting is seen to be confined to the eutectic areas, and is apparently due to the incomplete segregation of small nuclei of the constituent of higher melting point from the eutectic mixture. Until the percentage of tin in the mixture exceeds that represented by the point C in the curve (Diagram 1), the amount of eutectic visible in the polished plates is not proportional to each addition of tin made. When this point is passed a general proportion between the two may be stated to exist.

Putting together the evidence from the curves, the hydrogen evolutions (Diagram 2) and the microscopic structure, it may be concluded that there is a substance or series of substances present in these alloys marked by the common property of evolving hydrogen from water. The only very marked interruption to the continuity of the curve is in the region CD in the vicinity of an alloy corresponding to the formula AlSn . In the fluid mixtures containing larger percentages of aluminium than 18.5, there are more atoms of aluminium than of tin. From these media there appears to separate at successively lower temperatures solid matter which contains aluminium and tin in the proportions Al_xSn_y , where the value of x is at first greater than y , but is gradually approximating to it. This separation is taking place from a fluid which always contains more atoms of aluminium than of tin. The

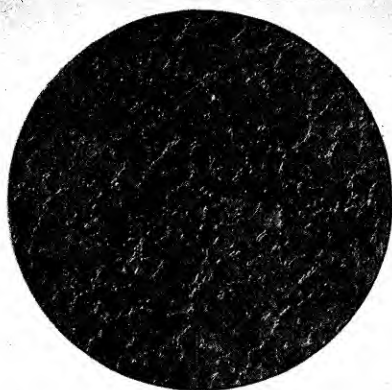
final member of this series of solids has the composition AlSn , and begins to fall out from a solution of the same composition at 561°C . The line ABCD connects the upper limits at which the separation of solid matter takes place in fluid mixtures containing excess of aluminium atoms. The line HKL marks the lower limit at which in our experiments this separation was active. Within the area ADLKH the mixture consists of solid, so-called aluminium-rich constituent, by which is to be understood solid containing not less than one atom of aluminium to one atom of tin, along with liquid of approximately the same composition. From mixtures containing about 18.5 per cent. of aluminium and lower proportions than that the last member of the former series AlSn is being separated from a fluid medium which contains excess of tin atoms, and the solution is thereby gradually impoverished in respect of aluminium until at the eutectic point, 228.73° (Heycock and Neville), it retains only about 0.48 per cent. of that constituent.

The existence of the compound AlSn as the terminal member of a series of bodies separating out from the fluid mixtures of aluminium and tin is inferred from the flattening of the liquidus curve at the part CD, in the vicinity of an alloy of this composition, and the small amount of heat liberated in mixtures richer in tin than AlSn as indicated by the liquidus and solidus curves approximating closely to one another to the right of that point.

The part of the curve from F to the eutectic point G has not been systematically examined by us, but analyses which we made on the fusible portion of the alloys which is automatically expressed at higher temperatures than the eutectic point, prove that the solvent power of tin for aluminium becomes appreciably greater as the temperature is increased. The liquid metal squeezed out between 300° and 400°C . is a solution, when liquid, containing 3 to 4 per cent. of aluminium. The ingots of composition $\text{Al} = 42.5$ per cent.; 15.4 per cent.; 8.04 per cent., yielded at 400°C . respectively beads of composition

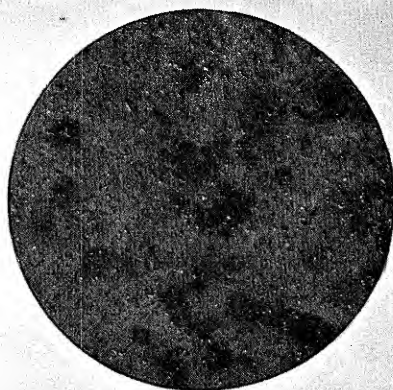
$$\text{Al} = 3.50 \text{ per cent.} : 3.76 : 3.52.$$

The saturated solution of aluminium in tin at 400° contains therefore 3.59 per cent. of aluminium, equivalent to 1 part AlSn dissolved in 5 parts of the solvent medium having the composition of the eutectic (0.48 per cent. Al). The segregation resulting on very slow cooling of these beads of saturated solution causes the very fluid eutectic residue to be extruded in some cases so as to cover the solid bead with an appendage of fine metallic hairs. The extent of this segregation will be indicated by continuing the line LM in the curve to meet EFG at the eutectic temperature G. The ease with which the compound AlSn , aluminium stannide, becomes oxidised, makes it impossible so far to isolate it from the metallic mixture in which it is produced.



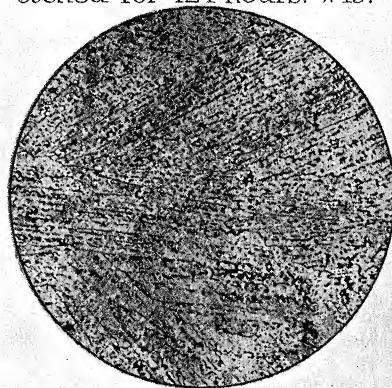
N° 1.

Al. 65%. Annealed & water-
etched for 124 hours. $\times 19$.



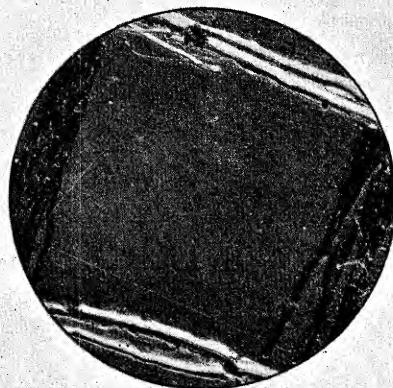
N° 2.

Al. 51.8%. Cast. $\times 19$. Oblique Illum.



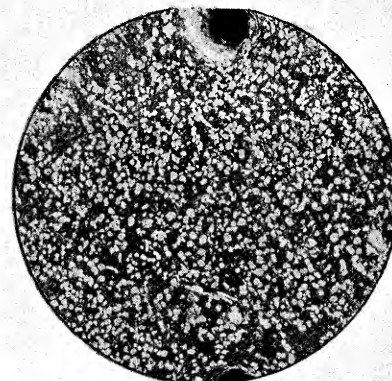
N° 3.

Al. 51.8%. Annealed. $\times 19$. Oblique Illum.



N° 4.

Al. 15.42%. Cast. Annealing Expt.
Oblique Illum. $\times 19$.



N° 5.

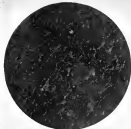
Al. 15.42%. Annealed at 300° C.
Oblique Illum. $\times 19$.



N° 6.

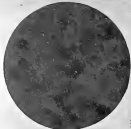
Al. 42.5%. Annealed. $\times 270$.
Nacht Prism.

J.P. Collins



Nº 1.

Al. 65%. Annealed & water-
etched for 124 hours. $\times 19$.



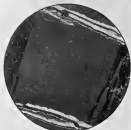
Nº 2.

Al. 51-6%. Cast. $\times 19$. Oblique Illum.



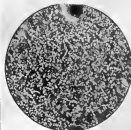
Nº 3.

Al. 51-6%. Annealed. $\times 19$. Oblique Illum.



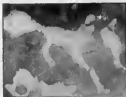
Nº 4.

Al. 15-42%. Cast. Annealing Expt.
Oblique Illum. $\times 19$.



Nº 5.

Al. 15-42%. Annealed at 300° C
Oblique Illum. $\times 19$.



Nº 6.

Al. 42-5%. Annealed. $\times 270$.
Nacht Prism.